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Phase transition and high-pressure elastic behavior of copper halides

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The phase-transition pressures of copper halides (CuCl, CuBr, and CuI) have been computed by employing the minimization technique of Gibbs free-energy expressed as a function of pressure and charge transfer (or three-body interactions) caused by the overlap of electron shells of the adjacent ions. We have also investigated the equation of state, which shows an appreciable volume collapse at the phase-transition pressures. The calculated values for the phase-transition pressures and the associated volume collapses are generally in excellent agreement with their measured data. The pressure variations of the elastic constants (C_{11}, C_{12}, and C_{44}) and their combinations have been found to vary such that the values of C_{11}, C_{12}, B_T $[=\frac{1}{3}(C_{11}+2C_{12})]$, and C_L $[=\frac{1}{2}(C_{11}+C_{12}+2C_{44})]$ increase with pressure, while those of the shear moduli C_{44} and C_S $[=\frac{1}{2}(C_{11}-C_{12})]$ decrease with it for all the copper halides. This feature is consistent with that observed in CuCl.

I. INTRODUCTION

The study of the covalent-ionic phase transition in copper halides (CuCl, CuBr, and CuI) has become the subject of increasing interest in recent years.[1-5] At ambient temperature and pressure these halides possess the zinc-blende (ZB) structure and behave as semiconductors with electronic structure similar to that of the tetrahedrally coordinated II-VI and III-V compounds of A^NB^{8-N} type, if the Cu 3*d* states are localized. They behave as superionic conductors at elevated temperatures[6,7] and exhibit an ionic conductive phase at high temperatures.[8] Also, they become nonconductive at extremely low temperatures.[9] Due to lack of inversion symmetry their properties are somewhat peculiar as compared with those of the alkali halides. A survey of the literature reveals that in recent years most of the theoretical[10-14] and experimental[15-20] investigators have paid attention to the study of dynamical, dielectric, thermal, and anharmonic properties of these materials and their mixed compounds.

Recently, the phase-transition pressures have been measured by means of the diamond envil cell[2] and x-ray absorptions[5] techniques and found to transform from zinc-blende (ZB) to rocksalt (RS) structure at ~10.5, 9.0, and >7.5 GPa for CuCl, CuBr, and CuI, respectively. Besides, these halides undergo a number of structural phase transitions[2-4] under pressure before attaining the ionic RS structure. An attempt has been made by Chelikowsky[1] to predict the ZB→RS phase-transition pressures by means of an *ab initio* pseudopotential total energy (PTE) method. He has obtained the corresponding values to be 6.35, 3.69, and 2.51 GPa for CuCl, CuBr, and CuI, respectively.

The pressure variations of the elastic constants (C_{11}, C_{12}, and C_{44}) and their combinations $[C_L=(C_{11}+C_{12}+2C_{44})/2]$ and shear modulus $[C_S=(C_{11}-C_{12})/2]$ have been measured by Hanson *et al.*[19] It is interesting to note that both Chelikowsky[1] and Hanson *et al.*[19] have expressed the necessity of including the effects of the charge-transfer mechanism in order to improve the theoretical predictions of the phase transition and the elastic behavior of copper halides. The effects of such a charge-transfer mechanism, leading to the existence of three-body interactions, has been successfully investigated by Singh and co-workers[21,22] in II-VI and III-V compound semiconductors[21] and divalent metal oxides.[22] This three-body potential (TBP) model has yielded somewhat better estimates of the phase-transition pressures, the volume collapses, the pressure variations of the elastic constants, and the anharmonic properties of these materials. We have earlier used this TBP model for a successful description of the anharmonic elastic properties[13] (namely, third-order elastic constants and the first- and second-order pressure derivatives of the second-order elastic constants) of CuCl, CuBr, and CuI.

Motivated by the above-mentioned versatility and remarkable successes[13,21,22] of the TBP model and the remark of Chelikowsky[1] and Hanson *et al.*,[19] we thought it pertinent to employ this TBP approach for the description of the phase-transition pressures, the equation of state, and the pressure variations of elastic constants of copper halides. The results of them have been obtained for the first time from the TBP model and they are in closer agreement with their experimental data[2,5,19,23] as compared to those obtained by earlier investigators.[1] We have also depicted the phase diagrams (e.g., equation of state) for evaluating the volume changes which show an abrupt volume discontinuity at the transition pressure leading to the volume collapse, $\Delta V(P_t)/V(0)$.

The essentials of the present theory and the methods of computations are described in Sec. II. The results obtained by us are presented in Sec. II and discussed in Sec. III.

II. THEORY AND METHOD OF COMPUTATIONS

The pressure causes change in the volume of a crystal and consequently it gives rise to the charge-transfer[24] [or three-body interactions (TBI)] due to the increase in the overlap of the neighboring electron shells. The stability of a lattice is attained at the minimum Gibbs free energy G ($=U+PV-TS$). Here, U is the internal energy equivalent to the lattice energy at 0 K. S is the vibrational entropy at absolute temperature T and V is the volume at pressure P. At temperatures sufficiently near zero (i.e., $T=0$) one can ignore[5,21,22] the entropy term (TS) and express it as

$$G_{B3}(r)=U_{B3}(r)+3.08r^3P \tag{1}$$

for the zinc-blende ($B3$) structure and

$$G_{B1}(r')=U_{B1}(r')+2.00r'^3P \tag{2}$$

for the rocksalt ($B1$) structure with lattice energies (U) defined as[13]

$$U_{B3}(r)=-\frac{\alpha_M e^2 Z}{r}[Z+2nf(r)]-\left[\frac{C}{r^6}+\frac{D}{r^8}\right]+b\sum_{ij}\beta_{ij}\exp[(r_i+r_j-r_{ij})/\rho] \tag{3}$$

$$U_{B1}(r')=-\frac{\alpha'_M e^2 Z}{r'}[Z+2n'f(r')]-\left[\frac{C'}{r'^6}+\frac{D'}{r'^8}\right]+b\sum_{ij}\beta_{ij}\exp[(r_i+r_j-r'_{ij})/\rho] \tag{4}$$

corresponding to the TBP model. The first term in them represents the Coulomb energy modified with TBI (Ref. 24) corresponding to the nearest-neighbor separations $r(r')$ and Madelung constants $\alpha_M(\alpha'_M)$ for ZB(RS) structures. Ze is the ionic charge and $f(r)$ is the TBI parameter dependent on the overlap integrals.[24] The second term is the van der Waals (vdW) energy due to dipole-dipole and dipole-quadrupole interactions with $C(C')$ and $D(D')$ as their overall coefficients estimated by us from the Slater-Kirkwood variational approach.[13] The last term is the Hafemeister-Flygare-type[13] repulsive energies due to the overlap of first- and second-neighbor ions. b and ρ are the hardness and range parameters with β_{ij} as the Pauling coefficients. $r_i(r_j)$ are the ionic radii of the cations (anions).

The TBP model approach we have described contains only three parameters [b, ρ, and $f(r)$] whose values can be evaluated from the knowledge of the equilibrium lattice energy, the elastic and lattice constants (2a), and the strategy adopted by us[13] elsewhere. The novelty in our calculations lies in the fact that we have not used any input data from its pressure-dependent properties which are intended for the prediction. The values of the input data and model parameters have been directly taken from Ref. 13 and reported here in Table I for ready reference. These parameters in the earlier paper[13] have been used to study only the anharmonic elastic properties of copper halides.

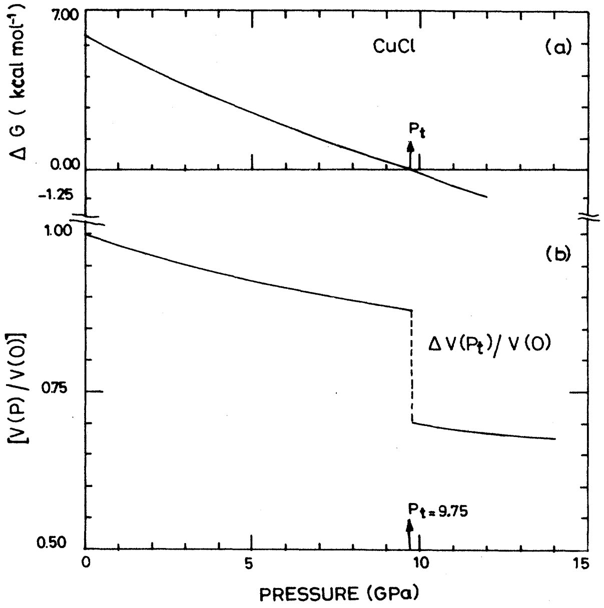

FIG. 1. (a) Variation of Gibbs free-energy difference (ΔG) with pressure (P); (b) variation of relative volume [$V(P)/V(0)$] with pressure (P) for CuCl.

In order to calculate the structural phase-transition pressures, we have minimized the lattice energies given by Eqs. (3) and (4) for the equilibrium interionic separations $r(r')$ for ZB(RS) phases. Their values have been reported in Table II. The corresponding Gibbs free energies G_{B3} and G_{B1} have been calculated from Eqs. (1) and (2) at different pressures (P). The variations of the Gibbs free-energy differences ΔG [$=G(B1)-G(B3)$] with pressures (P) have been depicted in Figs. 1(a), 2(a), and 3(a) for copper halides. The pressure at which ΔG tends to zero corresponds to the phase-transition pressure (P_t) as shown by arrows in these figures and their values are reported in Table III and compared with the available experimental[2,5,19,23] and other theoretical[1] results.

The calculated values of relative volumes, $V(P)/V(0)$,

TABLE I. Input data and model parameters for copper halides.

Property	$B_T(10^{10}\ \mathrm{N\,m^{-2}})$	Input data ϕ(kcal/mol)	$r(10^{-1}\ \mathrm{nm})$	Calculated model parameters $b(10^{-19}\ \mathrm{J})$	$\rho(10^{-1}\ \mathrm{nm})$	$f(r)$	Ref.
CuCl	39.30	232.00	2.34	0.521	0.283	−0.024	13
CuBr	38.87	227.90	2.40	0.523	0.298	−0.027	13
CuI	35.50	225.88	2.62	0.530	0.313	−0.035	13

TABLE II. Lattice parameters and relative stability of copper halides.

Crystal	Equilibrium separation $r(10^{-1}$ nm) (Expt.)[a]	$r'(10^{-1}$ nm)	Lattice energy (kcal/mole) $U(B3)$ (Expt.)[a]	$U(B1)$	ΔU $[=U(B1)-(B3)]$ (kcal/mole)
CuCl	2.34 (2.34)	2.46	(−232.00)	−225.78	6.22
CuBr	2.46 (2.46)	2.51	(−227.90)	−226.26	1.64
CuI	2.62 (2.62)	2.76	(−225.80)	−223.61	2.68

[a] Reference 13.

associated with compressions have also been obtained and plotted versus the pressures to depict the phase diagrams in Figs. 1(b), 2(b), and 3(b). The percentage of the relative volume collapse $[\Delta V(P_t)/V(0)]$ at the phase-transition pressure (P_t) has also been presented in Table III.

The pressure variations of the second-order elastic constants SOEC's (C_{11}, C_{12}, and C_{44}) and their combinations, C_L, C_S, and B_T $[=(C_{11}+2C_{12})/3]$ have been obtained for both ZB and RS phases and depicted in Figs. 4–7. The expressions for these elastic constants for the TBP model are the same as those given in our earlier papers.[13,21] The results obtained by us are discussed in the following section.

III. DISCUSSIONS AND CONCLUSIONS

A look at Table II reveals that the present TBP model has correctly predicted the relative stability of the competitive phases in all the cases as the values of ΔU $[=U(B1)-U(B3)]$ are positive, which is a required criterion.[21,22] Also, the values of the equilibrium separations (r) obtained by us from the minimization technique are in good agreement with their experimental data.[2,19]

It is obvious from Figs. 1–3(a) that the energy differences (ΔG) have attained their values to be zero at the phase-transition pressure ($P_t=9.75$, 8.2, and 8.5 GPa) for CuCl, CuBr, and CuI, respectively. These values are in better agreement with their measured data[2,5,23] ($P_t=\sim 10.5$, 9.0, and >7.5 GPa) than those obtained by Chelikowsky.[1] Also, there is an abrupt change in Figs. 1(b), 2(b), and 3(b) of volume discontinuity at the phase-transition pressures showing the compression of the lattice due to which the ZB structure becomes unstable at high pressures and transforms to a denser phase, i.e., sixfold coordinated structures. The copper halides are the most ionic materials in the semiconductor family and hence eventually reach the RS structure.[1]

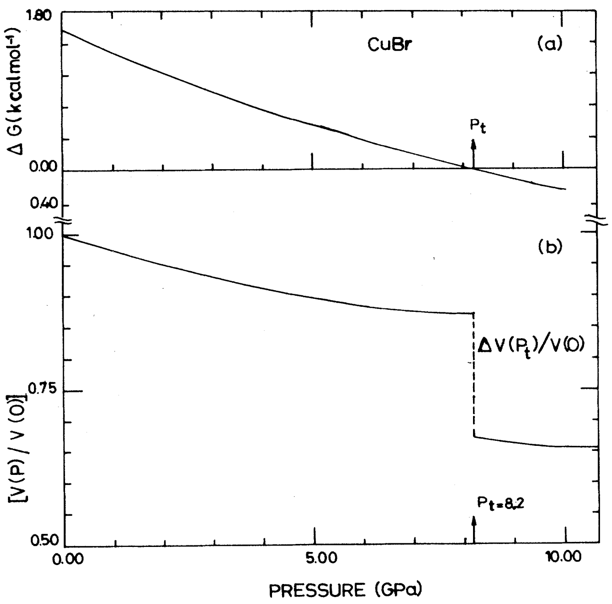

FIG. 2. (a) Variation of Gibbs free-energy difference (ΔG) with pressure (P); (b) variation of relative volume $[V(P)/V(0)]$ with pressure (P) for CuBr.

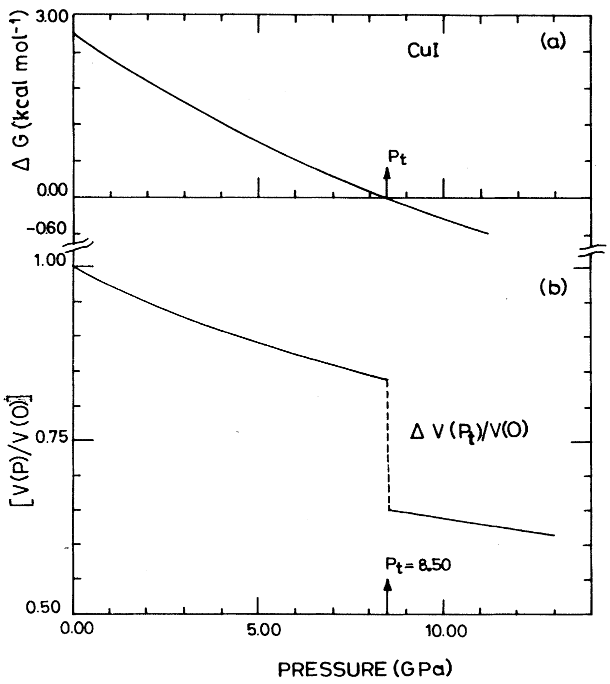

FIG. 3. (a) Variation of Gibbs free-energy difference (ΔG) with pressure (P); (b) variation of relative volume $[V(P)/V(0)]$ with pressure (P) for CuI.

TABLE III. Transition pressure (P_t) and percentage relative volume collapse at P_t [$\Delta V(P_t)/V(0)$] for copper halides.

Crystals	Phase-transition pressure (P_t) (GPa) Expt.[a]	Present	Others[b]	Percentage of relative volume collapse at P_t [$\Delta V(P_t)/V(0)$] Expt.	Present	$V(P_t)/V(0)$
CuCl	6.0– ~10.5	9.75	6.35	11[c]	18.65	0.883
CuBr	6.6–9.0 8.3–8.7	8.2	3.69	14[d]	19.75	0.870
CuI	>7.5–15.0	8.5	2.51	15[e]	19.00	0.841

[a] References 2–5.
[b] Reference 1.
[c] Reference 23; the values are at 6.0 GPa and at room temperature.
[d] Reference 23; the values are at 6.6 GPa and at room temperature.
[e] Reference 23; the values are at 8.0 GPa and at 100 °C.

The relative success achieved in predicting the phase-transition pressures and the volume collapses can be ascribed to the inclusion of the vdW interactions and the charge-transfer (or three-body) effects as envisaged by Chelikowsky[1] and others.[13,19] The better predictions achieved from the TBP model over the PTE approach might be due to the fact that the later approach is inadequate to account for the Cauchy violation in these crystals.

The volume collapses listed in Table III are within the criterion of Phillips[25] (19±2% for covalent-ionic transition) and they are comparable with experimental[23] and

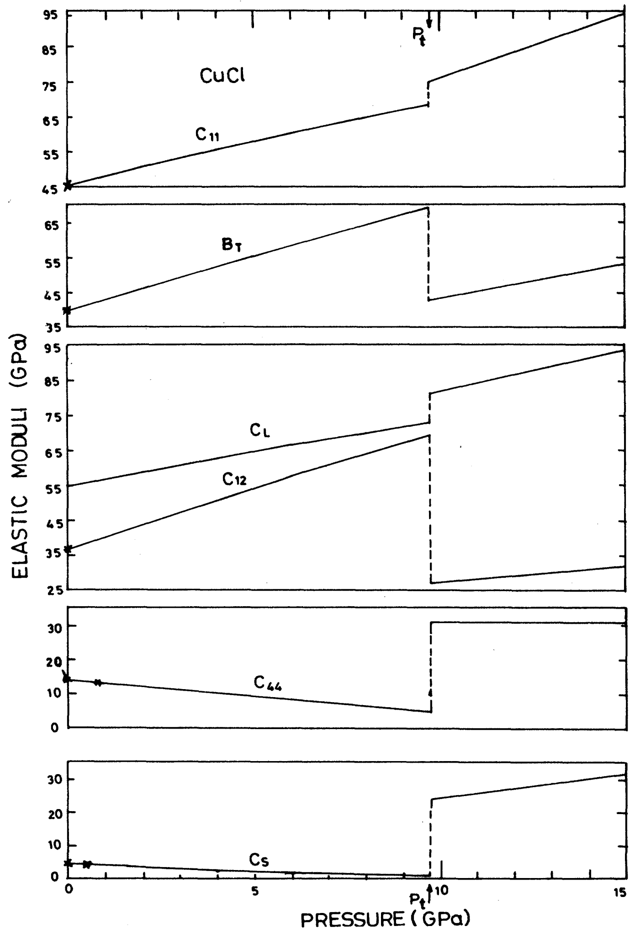

FIG. 4. Variation of elastic moduli with pressure (P) for CuCl; the crosses (×) are the experimental signs from Ref. 19.

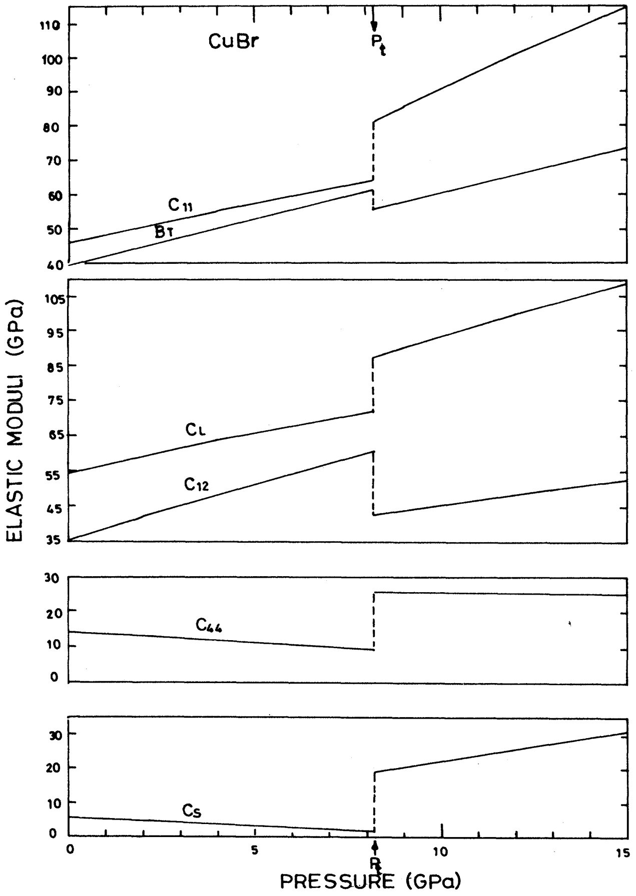

FIG. 5. Variation of elastic moduli with pressure (P) for CuBr.

other theoretical[21] results on semiconductors. Also, the TBP model has been used to reveal the ratio of normalized volumes $[V(P_t)]$ to initial volume $[V(0)]$ listed in Table III.

In order to study the high-pressure elastic behavior of the copper halides, we have estimated the pressure variations of the SOEC's (C_{11}, C_{12}, and C_{44}) and their combinations (C_L, C_S, and B_T) and depicted them in Figs. 4–7. It is noted from these figures that both the shear moduli (C_S and C_{44}) decrease linearly up to the phase-transition pressure and show an abrupt change at P_t beyond which the C_S increases while C_{44} becomes almost constant. In order to demonstrate the effectiveness of the TBI model to predict the pressure variations of the shear moduli (C_S and C_{44}) at lower pressures, we have plotted such variations in an extended form in Fig. 7 in the range of pressure from 0 to 1.0 GPa and found them to agree fairly well with the available experimental data for CuCl.[19]

In the case of CuCl, C_S attains almost zero value at P_t and this feature is in agreement with the experimental results.[19] The decrease in the shear moduli shows that the phase transition in these halides is accompanied by the shear deformation arising due to the lattice instability and is consistent with the conclusions drawn by others.[5,19,23] This decrease in shear constants with applied pressure reflects the strong weaking of the bonding force constant in these crystals. This weaking of bonding force constant may be an indication that the crystals are becoming more ionic with decreasing lattice separation. The elastic constants C_{11}, C_{12}, B_T, and C_L, on the other hand, increase with pressure. At the phase-transition pressures, it is seen from Figs. 4–6 that all the SOEC's (C_{11}, C_{12}, B_T, and C_L) increase linearly up to P_T and show steep decrease at P_t in C_{12} and B_T. In contrary, there is an abrupt increase in C_{11} and C_L at P_t. However, all these SOEC's increase linearly beyond the phase-transition pressure. It is obvious from Figs. 4–6 that while going from the ZB to the RS phase all the elastic constants show an abrupt change at the phase-transition pressure. The lattice parameters have been found to decrease with pressure (although not shown or reported in this paper), but at P_t it shows an abrupt increase and after that it again decreases linearly. This feature of lattice parameter is also consistent with the available experimental information as discussed by Livescu and Brafman[12] and Meisalo and Kalliomaki.[23]

In Figs. 4–6, we have considered only ZB and RS phases of the copper halides for studying the pressure variations of the elastic constants as the system in both these phases has fcc unit cells. However, the copper

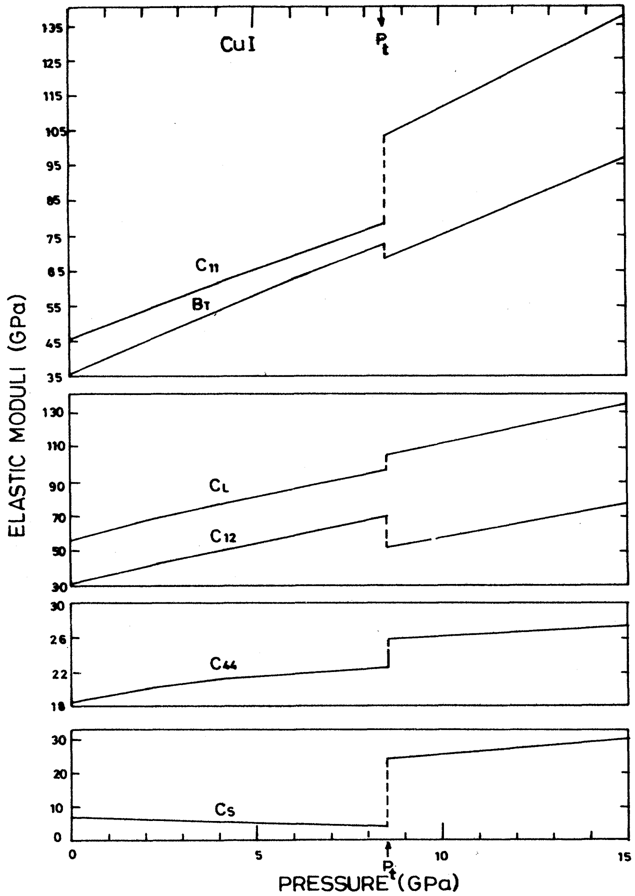

FIG. 6. Variation of elastic moduli with pressure (P) for CuI.

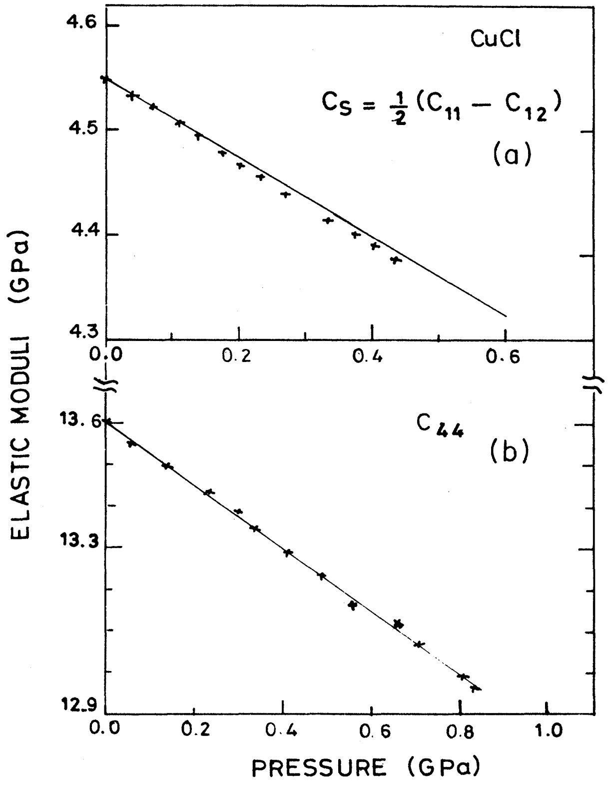

FIG. 7. Variation of shear moduli (C_S and C_{44}) with pressure (P) in range of 0 to 1.0 GPa for CuCl. The crosses (×) correspond to the experimental data.[19].

halides undergo a number of phase transitions[2-4] (such as tetragonal, hexagonal, and rhombohedral) in between the pressures from 0 to 12 GPa. The variations presented in Figs. 4–6, lacking such details of changing phases with pressure variation of elastic constants, are the first reports; they are of only academic interest at present but they will serve as a guide to experimental workers in the future.

In view of the overall achievements, it may be concluded that the TBP model is capable of describing the high-pressure behavior of the copper halides almost with the same success as it has done in the cases of II-VI and III-V semiconductors[21] and divalent metal oxides.[22] This approach, being relatively simpler, has a promise to reveal the high-pressure phase transformation and elastic properties of binary ionic solids.

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